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Cation ordering in Ni–Fe olivines

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Abstract

Synthetic nickel–iron olivines, equilibrated at 1000°C, were investigated by means of Mössbauer spectroscopy at high and low temperature. A strong tendency towards an ordering of Ni^{2+} into the M1 site and Fe^{2+} into M2 was observed. K_D for the exchange reaction $Ni^{2+}(M1) + Fe^{2+}(M2) \rightleftarrows Fe^{2+}(M1) + Ni^{2+}(M2)$ varies little with chemical composition, suggesting a near ideal solid solution in Ni–Fe olivines. Gibbs free energy of exchange at 1000°C is calculated to be 6.0 kcal/mole (24.9 kJ/mole).

Introduction

Nickel is an important constituent which usually fractionates into olivine in early magmatic crystallization (Wager and Mitchell, 1951). Olivines containing nickel are usually found in ultramafic rocks of possible upper-mantle origin. The most nickel-rich olivine, liebenbergite, with composition $(Ni_{1.52}Mg_{0.33}Co_{0.05}Fe_{0.12})SiO_4$, has been described by de Waal and Calk (1973). Nickel-bearing olivine is usually Mg-dominant, although a complete solid solution of Ni_2SiO_4 and Mg_2SiO_4 was observed by Akomoto *et al.* (1976). In most natural olivines, however, iron is the second most important solid solution constituent. This paper reports on an investigation of the Ni_2SiO_4–Fe_2SiO_4 solid solution.

The potential use of intracrystalline order–disorder among the non-equivalent M1 and M2 sites in olivines for estimating rock-forming temperature provides incentive for studying the distribution within this mineral (see *e.g.*, Brown, 1980). The intracrystalline Fe–Mg distribution in olivines is still in debate and has been observed to be temperature dependent by Virgo and Hafner (1972) and Finger and Virgo (1971), or dependent on oxygen fugacity as suggested by Will and Nover (1979). A third possibility is the influence of a third element, for example Ni.

Studies of solid solutions of transition elements such as Ni (Rajamani *et al.*, 1975; Wood, 1974; Bish, 1981), Co (Ghose and Wan, 1974), and Zn (Brown, 1970) in forsterite have shown an enrichment of these elements into the M1 site, whereas Mn (Francis and Ribbie, 1980) fractionates into the M2 sites in olivines. The observed cation ordering is explained in part by the crystal field stabilization energy criteria (CFSE) or, for ions yielding zero CFSE (Mn,Zn), by ionic size criteria or covalency effects. In the present study, Ni^{2+} and Fe^{2+} are both affected by the crystal field, predicting a less ordered distribution in Ni–Fe olivines than in Ni–Mg olivines. On the other hand, according to the ionic size criteria, the difference in the ionic radii (Fe^{2+} = 0.77, Ni^{2+} = 0.70Å) suggests an ordering of Ni^{2+} into the smaller M1 site. the observed fractionation of certain transition metal ions, usually observed in minor amounts in natural olivines, may be partly responsible for the observed variations in element distribution in natural Fe–Mg olivines.

Synthesis and experimental results

Synthetic olivines were produced from oxide mixtures (*p.a.* grade SiO_2, Fe_2O_3, metallic Fe and NiO). Crystallization of olivines was performed with the mixtures in gold capsules in an internally heated autoclave for 140 hours at 1000°C (pressure: 1.0±0.1 kbar) using argon as pressure medium. Samples H 11 and H 12 were crystallized from melts held at ~2000°C in an arc furnace in an argon atmosphere, and were afterwards annealed at 1000°C for 168 hours in evacuated silica tubes ($<10^{-3}$ torr) and quenched to room temperature.

Optical examination of the products showed the presence of trace amounts of opaque phases (magnetite, Ni–Fe alloy) and of quartz in some runs. The opaque phases were carefully removed under acetone by use of a hand magnet. X-ray diffraction

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analysis and Mössbauer spectroscopy studies later show no sign of impurities remaining in the samples. Cell parameter refinements (Table 1 and Fig. 1) on the synthetic olivines were performed with X-ray powder diffraction data (13 to 26 reflections) using a computer program (CELNE) assuming space group *Pbnm*. The crystal size obtained from the synthetic runs was large enough (~10 μm) to allow microprobe analysis of at least three grains from each run. Values given in Table 1 are average values, obtained from computer corrected data. Within the limit of the analyzing technique no significant zoning or inhomogeneity of the olivine grains was observed.

Mössbauer spectra of powder samples were obtained with the absorber held at an elevated or low temperature. This increases the resolution of the absorption pattern arising from ^{57}Fe in M1 and M2 sites (Bush *et al.*, 1970; Kündig *et al.*, 1967). The temperature was regulated within ±1°. Spectra were accumulated in a multichannel analyzer (512 channels) operating in multi-scaling mode. The electro-mechanical vibrator was driven with a constant magnitude of acceleration and the mirror symmetric spectra were folded and summed before the computer analysis (Agresti *et al.*, 1969). Co in Rh was used as a source, always at room temperature, and centroid shifts are given relative to metallic Fe. Mössbauer results are shown in Table 2.

The occupation of Fe at the M1 and M2 sites is obtained from the area ratios (Table 3) of the computer fitted Mössbauer spectra (Figs. 2 and 3).

Table 1. Composition and cell parameters of synthetic olivines

	17	H 14	15	16	H 11	H 12
SiO_2 wt-%	29.5	28.8	29.7	29.3	28.2	28.3
FeO	71.8	63.5	61.1	58.2	34.9	17.4
NiO	0.0	6.5	8.5	12.6	33.9	53.8
Σ	101.3	98.8	99.3	100.1	97.0	99.5
Number of ions on the basis of 4 oxygens						
Si	0.99	0.99	1.01	1.00	1.00	0.99
Fe^{2+}	2.02	1.83	1.74	1.66	1.03	0.51
Ni	0.00	0.18	0.23	0.35	0.97	1.51
X^{Fe}	1.00	0.91	0.88	0.83	0.52	0.25
X^{Ni}	0.00	0.09	0.12	0.17	0.48	0.75
Cell parameters (space group Pbnm)						
a Å	4.821(1)	4.807(1)	4.797(1)	4.788(1)	4.779(6)	4.738(1)
b	10.478(2)	10.457(2)	10.447(3)	10.437(2)	10.335(5)	10.241(2)
c	6.092(2)	6.078(2)	6.075(2)	6.066(1)	6.019(5)	5.976(1)
V $Å^3$	307.7	305.5	304.4	303.1	297.3	290.0

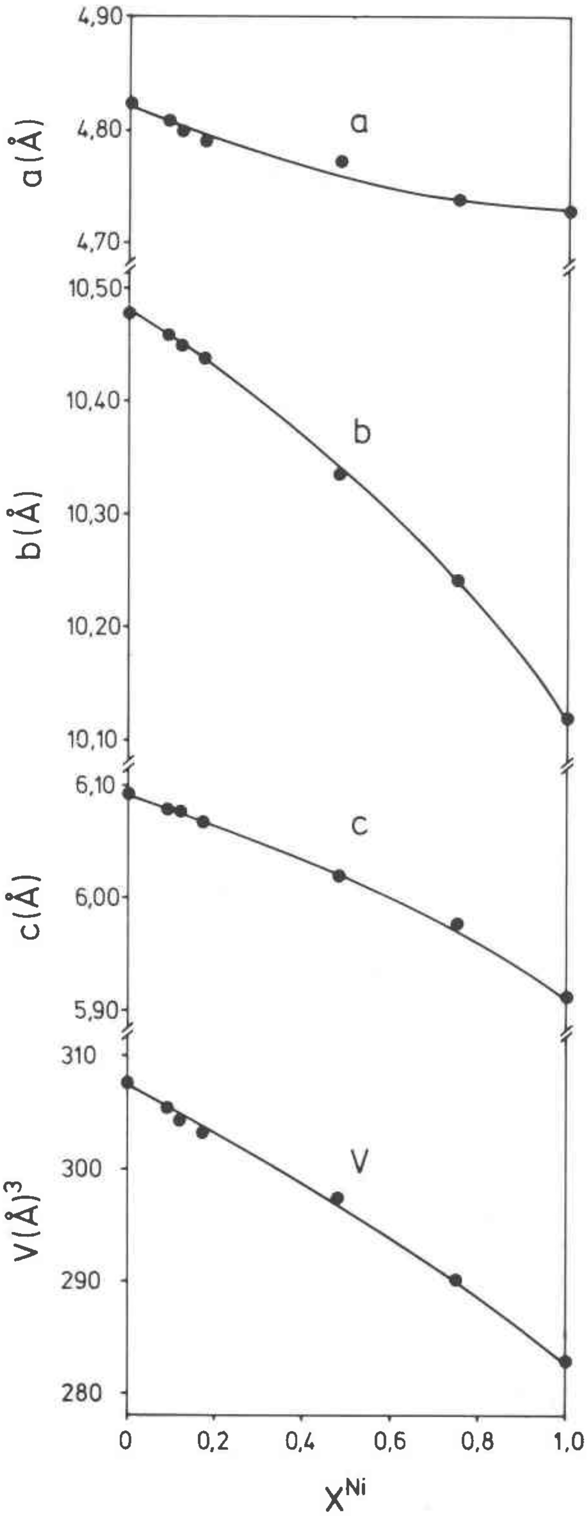

Fig. 1. Cell parameter variations with composition of synthetic Ni–Fe-olivines. Values for Ni_2SiO_4 from Brown (1970).

Table 2. Mössbauer parameters of ^{57}Fe in synthetic olivines

Sample	T,K	H_{eff}		IS		ΔE_Q		Width
		M1	M2	M1	M2	M1	M2	
17	6	31.8	12.1	1.29	1.32	3.27	3.05	0.38
17	540	0	0	0.91	0.98	1.99	2.47	0.24
17	673	0	0	0.83	0.90	1.76	2.25	0.24
H 14	673	0	0	0.83	0.90	1.78	2.26	0.24
15	673	0	0	0.83	0.89	1.78	2.25	0.26
16	6	nd	12.3	nd	1.33	nd	3.13	0.35
16	680	0	0	0.82	0.89	1.77	2.22	0.25
H 11	9	nd	12.3	nd	1.33	nd	3.10	0.38
H 11	673	0	0	0.83^x	0.91	1.98	2.28	0.32
H 12	6	-	12.1	-	1.34	-	3.09	0.50
H 12	820	-	0	-	0.79	-	1.95	0.29

H_{eff} given in Tesla. IS, ΔE_Q and Width given in mm/s (±0.01).
IS given relative to metallic iron at room temperature.
^{x} constrained

Table 3. Site occupancy in synthetic olivines

Sample	T,K	X_{01}^{Fe}	Area %		X^{Fe}		
			M1	M2	M1	M2	K_D
17	6	1.00	49.2	50.8			
17	560	1.00	49.5	50.5			
17	673	1.00	48.6	51.4	1.00	1.00	
H 14	673	0.91	45.4	54.6	0.87	0.99	0.07(3)
15	673	0.88	43.2	56.8	0.77	0.96	0.14(3)
16	6	0.83	~30	~70			
16	680	0.83	40.4	59.6	0.69	0.96	0.09(3)
H 11	9	0.52	~10	~90			
H 11	673	0.52	23.1	76.9	0.24	0.80	0.08(4)
H 12	6	0.25	~0	~100	~0	0.25	~0.00
H 12	820	0.25	~0	~100	~0	0.25	~0.00

$$K_D = \frac{X_{M1}^{Fe} \cdot (1-X_{M2}^{Fe})}{X_{M2}^{Fe} \cdot (1-X_{M1}^{Fe})}$$

Assignments of the ^{57}Fe resonance pattern are made in agreement with Warburton (1978), Kündig *et al.* (1967), Karyagin (1966), and van Dongen Tornman *et al.* (1975). High-temperature spectra have been corrected for different recoil-free fractions of iron in the M1 and M2 sites. The M1 pattern in the low-temperature spectra is considerably broadened with increasing Ni-content, making precise determination of the Mössbauer parameters very difficult. However, as seen from Figure 3, the M1 pattern is completely lacking in the most iron-poor sample H 12.

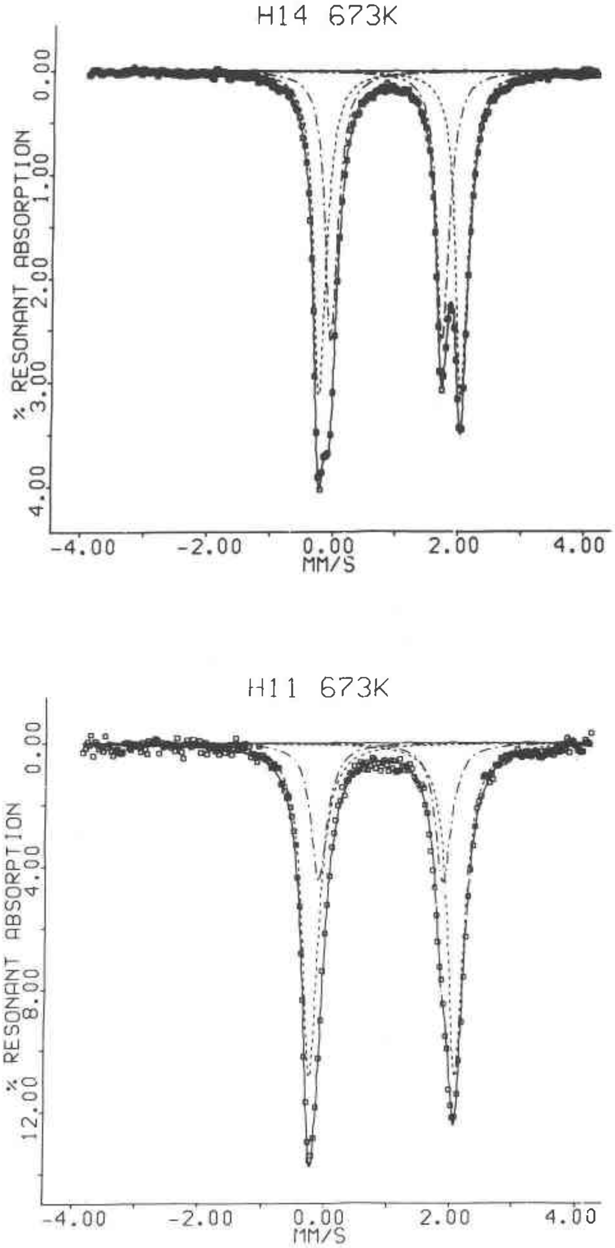

Fig. 2. Mössbauer spectra of samples H 14 and H 11 at 673 K. -·- M1 site, --- M2 site.

Discussion

Ni–Fe distribution in olivine

The almost linear decrease in volume with increasing Ni-content in fayalite indicates a small deviation from Vegard's law. The slight increase in the slope of the volume change beyond $X^{Ni} = 0.5$ may suggest an increasing substitution of the small Ni^{2+} ion into the larger M2 site in olivine. This is further supported by the distribution coefficients (K_D) obtained from the Mössbauer spectra (*cf.* Table 3). K_D for ionic distribution of Fe^{2+} and Ni^{2+} between the two non-equivalent sites is defined by:

$$K_D = \frac{X^{Fe}_{M1}\,(1 - X^{Fe}_{M2})}{X^{Fe}_{M2}\,(1 - X^{Fe}_{M1})}$$

The observed K_D-values indicate a strong preference for Ni^{2+} to enter the M1 site in competition with Fe^{2+} in olivine.

The intracrystalline exchange in Ni–Fe olivine may be expressed by the following reaction

$$Ni^{2+}(M1) + Fe^{2+}(M2) \rightleftarrows Ni^{2+}(M2) + Fe^{2+}(M1)$$

with the following equilibrium constant:

$$K_a = \frac{a^{Fe}_{M1}\cdot a^{Ni}_{M2}}{a^{Fe}_{M2}\cdot a^{Ni}_{M1}}$$

The small variation in the observed values of K_D (*cf.* Table 3) for different compositions in olivine may indicate that the activity coefficient approaches unity and the solid solution of Fe^{2+} and Ni^{2+} in olivine is close to ideal, in agreement with earlier observations at elevated temperature (Saxena, 1973). K_D can therefore be set equal to K_a and the Gibbs free energy change $\Delta G° = -RT\ln K_D$, can be estimated from the observed distribution values. The calculated average value at 1000°C is 6.0 kcal/mole (24.9 kJ/mole). The observed high degree of ordering of the ions in Ni–Fe olivines is in good agreement with the prediction from ionic size criteria. They are markedly more ordered than Ni–Mg olivines as expected from the smaller difference between Mg^{2+} and Ni^{2+} ionic radii (Rajamani *et al.*, 1975). The strong influence on the distribution from ionic size differences is further supported by the observed intracrystalline distribution in Mn–Fe olivines, where the larger Mn^{2+} ion strongly fractionates into M2 in competition with the smaller Fe^{2+} ion (*cf.* Fig. 4).

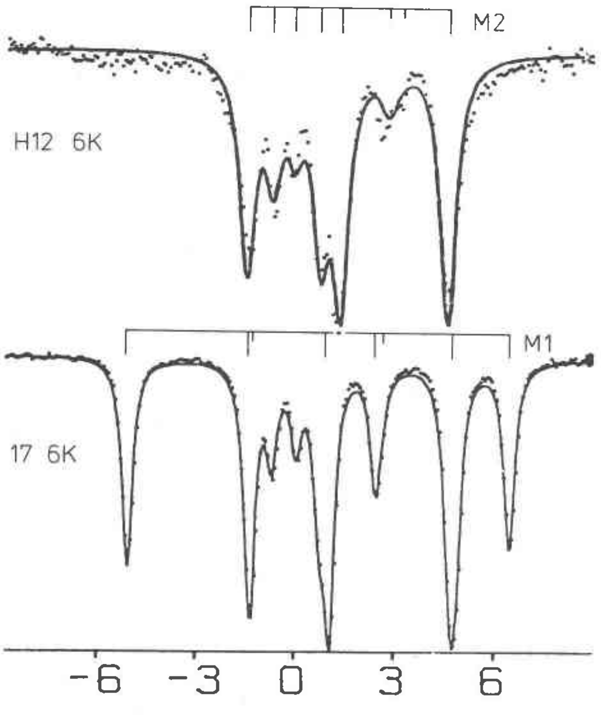

Fig. 3. Mössbauer spectrum of magnetically ordered olivine at 6 K. Upper spectrum sample H 12 with iron apparently only in M2. Lower spectrum sample 17 with both M1 and M2 equally populated by iron. Forbidden transitions shown by small bars.

Crystal field stability theory also predicts a strong ordering of Ni^{2+} into the M1 site (Burns, 1970). Indeed Walsh *et al.* (1974) suggested that Fe^{2+} gains extra CFSE at M2 by the dynamic Jahn–Teller effect from the trigonal distortion of the M2 site in olivine. This feature would then explain the increased ordering in Ni–Fe olivines relative to Ni–Mg olivines observed for synthetic olivines (Rajamani *et al.*, 1975; Bish, 1981). Bish (1981) also investigated a natural Ni–Fe–Mg-bearing olivine $(Ni_{1.52}Co_{0.05}Fe_{0.09}Mg_{0.32})SiO_4$ approaching our sample H 12 in composition. The natural sample (estimated equilibration temperature 730°C) was found to be fully ordered with the M1 site exclusively populated by Ni^{2+}. Our sample H 12, annealed at 1000°C, indicates a similar ordering.

Bonding of iron

Some quantitative data regarding the bonding of iron in Ni–Fe olivine are obtained from the Mössbauer parameters given in Table 2. Quadrupole splittings, sensitive to the near surroundings of the iron nucleus, generally increase with increasing nickel-content of the solid solutions, and are markedly more at the M1 site. This is in agreement with the expected smaller distortion of the M1 site with increasing occupancy by the smaller Ni^{2+} ion (Brown, 1980). At low temperature (6 K), however, the M1 site shows a larger splitting compared to the less distorted M2 site. The observed quadrupole splitting is a combined effect of the crystalline field, spin-orbit interaction and core polarization. The latter features are expected to change at low temperature close to absolute zero, thereby resulting in

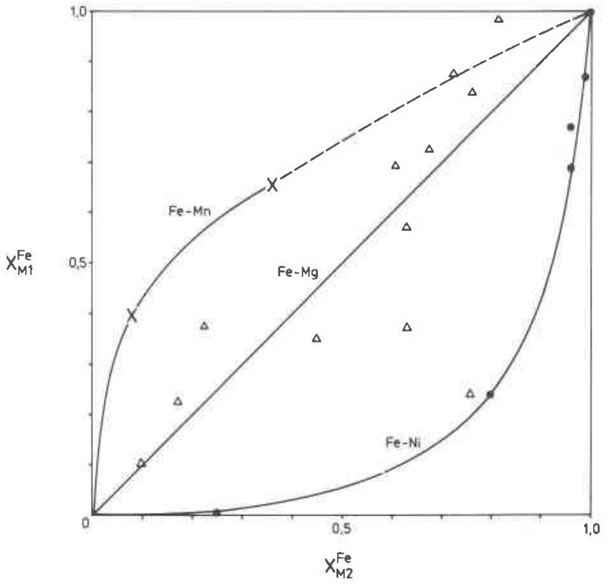

Fig. 4. Iron distribution in olivines. ● Fe–Ni-olivines (this study), △ Fe–Mg-olivines (Warburton, 1978), X Fe–Mn-olivines (Brown, 1970).

an increased quadrupole splitting. This effect should be markedly larger at a distorted site.

Isomer shifts are consistently smaller for iron in the M1 site. It can be expected that a decrease in the volume of the coordination polyhedron would lead to an increased electron density and hence, in the case of ^{57}Fe, a decrease in the value of the isomer shift (Tang Kai *et al.*, 1980).

Conclusions

Nickel orders highly preferentially into the M1 site in fayalite: the ordering is more pronounced than in forsterite of similar nickel-content. The difference in effective ionic radius between Fe^{2+} and Ni^{2+} is expected to be the dominant reason for the observed fractionation between M1 and M2 sites in olivine. Both ions are stabilized by the crystal field, however, and the observed ordering is in agreement with the observed crystal field stabilization energies for Ni^{2+} and Fe^{2+} in olivines. Evidence from the X-ray data and the observed compositional variation of the distribution coefficient (K_D) shows that the solid solution in Ni–Fe olivine is close to ideal at 1000°C.

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